

What is claimed is:

1. A sampling system for determining concentration of additives in a metal plating bath from an electrochemical processing tool, the system comprising:

- a) at least one analysis chamber;
- b) a sampling duct comprising a sampling inlet and at least one sample loop, wherein the sampling inlet is in fluid communication with the electrochemical processing tool for receiving a plating bath sample for analysis in the at least one analysis chamber;
- c) a four-way valve positioned between the sampling inlet and the electrochemical processing tool, wherein the plating bath sample is flowed through the four-way valve from the electrochemical processing tool into the sampling duct;
- d) at least one actuatable multi-port valve in fluid communication with the sampling duct;
- e) at least one carrier fluid duct in fluid communication with the analysis chamber, wherein the carrier fluid duct and sampling duct are in fluid communication via the actuatable multi-port valve;
- f) a flow sensor in fluid communication with the sampling duct and positioned downstream from the at least one actuatable multi-port valve, wherein the flow sensor measures a predetermined quantity of plating bath sample flowing through sample duct;

- g) a purging gas source in fluid communication with the four-way valve for introducing a purging gas source into the sampling duct between successive sample analyses; and
- h) a waste line in fluid communication with the four-way valve, wherein plating bath solution can be transferred from the processing tool through the four-way valve to the waste line.

2. The system according to claim 1, further comprising a valve control system for controlling the four-way valve to provide a first mode in which the plating bath sample is flowed from the processing tool into the sample duct, a second mode in which the plating bath sample from the processing tool is directed to the waste line, a third mode in which the purge gas source is introduced to the sample duct to purge plating bath sample from the sample duct, and a fourth mode in which the purging gas source is directed to the waste line.

3. The system according to claim 2, wherein the valve control system is communicatively connected to the flow sensor and the four-way valve, wherein the first mode of the four-way valve is turned off when the predetermined quantity of plating bath sample has been flowed through sample duct pass the flow sensor.

4. The system according to claim 2, wherein the plating bath sample is purged from the sample duct by actuating the four-way valve and introducing a purging gas into the sample duct.

5. The system according to claim 2, wherein the at least one actuatable multi-port valve has a first and second position, and wherein the first position provides for the plating bath sample to flow through the sample duct and the second position provides for flowing the plating bath sample in the sample loop into the carrier fluid duct to the analysis chamber.
6. The system according to claim 5, wherein the actuatable multi-port valve is in the first position for purging the sample duct with the purging gas source.
7. The system according to claim 5, wherein the plating bath sample in the at least one sample loop is flowed into the carrier fluid duct when the multi-port valve is actuated into the second position and the four-way valve is in the third mode.
8. The system according to claim 1, comprises at least two analysis chambers, at least two sample loops, at least two actuatable multi-port valves and at least two carrier fluid ducts.
9. The system according to claim 1, further comprising reagent containers for holding reagents that are introduced into the at least one analysis chamber.
10. The system according to claim 1, further comprising reagent containers for holding reagents that are introduced into the at least one analysis chamber and the carrier fluid duct.

11. The system according to claim 1, wherein the at least one of the sample loop contains from about 1 ml to about 10 ml of plating bath sample.
12. The system according to claim 1 which comprises two sample loops, wherein a first sample loop contains a smaller volume of plating bath sample than the second sample loop and both sample loops fill at approximately the same time.
13. The system according to claim 12, wherein the smaller fluid amount of plating bath sample is introduced into the analysis chamber from the sample duct through the actuatable multi-port valve and the carrier fluid duct.
14. The system according to claim 12, further comprising an auxiliary sample duct in fluid communication with the sample duct and analysis chamber, wherein the plating bath sample contained in the second sample loop is introduced into the analysis chamber through the auxiliary sample duct.
15. The system according to claim 1, further comprising a drain pump in fluid communication with the analysis chamber to drain used analysis solution from the analysis chamber.

16. The system according to claim 15, further comprising a liquid transferring system for refilling the analysis chamber with a primary electrolyte after draining used analysis solution from the analysis chamber.
17. The system according to claim 16, wherein the transferring system comprises an electrolyte fluid and a means of transferring a measured amount of electrolyte for transference to the analysis chamber.
18. The system according to claim 17, wherein the means for transferring a measured amount of the liquid comprises a syringe pump sized to increase transference load of the liquid.
19. The system according to claim 18, wherein the syringe pump comprises:
- a) a cylindrical housing sized to transfer at least 10 ml of liquid, wherein the cylindrical housing has an open first end and a closed second end;
  - b) a cylindrical plunger rod having a first and second end and slidably mounted within the cylindrical housing, wherein the second end of the plunger rod extends through the closed second end of the housing;
  - c) a tip comprising a body portion having a first and second tip end and a central bore therethrough wherein the first end of the tip is connected to the first end of the cylindrical housing, and wherein the second end has a bore diameter sized to

reduce back pressure when filling and reduce the formation of irreproducible droplets at the second end of the tip; and

d) a flexible sealing member connected to the first end of the plunger rod, wherein the flexible sealing member comprises three overlapping radial flaps to form a sealed chamber between the flexible sealing member and the second end of the tip, and wherein the sealed chamber holds a transferable liquid.

20. A system for determining additives in a metal plating bath in an electrochemical processing tool, the system comprising:

- a) at least one analysis chamber;
- b) a sampling duct comprising a sampling inlet and at least one sample loop positioned upstream from the sample inlet, wherein the sampling duct is in fluid communication with the processing tool for receiving a plating bath sample for analysis in the at least one analysis chamber;
- c) an inlet four-way valve positioned between the sampling inlet and the processing tool, wherein the inlet four-way valve is in fluid communication with the sample inlet, and wherein the plating bath sample is flowed through the inlet four-way valve from the processing tool into the sampling duct;
- d) at least one carrier fluid duct in fluid communication with the analysis chamber and sampling duct;

- e) at least one actuatable multi-port valve in fluid communication with the sampling duct and carrier fluid duct, wherein the at least one actuatable multi-port valve has a first and second position, and wherein the first position provides a flow path for flowing the plating bath sample through the sampling duct and the second position provides a flow path for flowing the plating bath sample from the sampling duct to the carrier fluid duct;
- f) a flow sensor in fluid communication with the sampling duct and positioned downstream from the at least one actuatable multi-port valve, wherein the flow sensor measures a predetermined quantity of plating bath sample flowing through sample duct and then triggers the actuation of the multi-port valve into the second position;
- g) a purging gas source in fluid communication with the four-way valve for introducing a purging gas source into the sampling duct to purge previous plating bath sample from the system;
- h) a waste line in fluid communication with the four-way valve, wherein plating bath solution is transferred from the processing tool through the four-way valve to the waste line;
- i) a valve control system for controlling the inlet four-way valve to provide a first mode in which the plating bath sample is flowed from the processing tool into the sample duct, a second mode in which the plating bath sample from the processing tool is directed to the waste line, a third mode in which the purge gas source is

introduced to the sample duct to purge plating bath sample from the sample duct, and a fourth mode in which the purging gas source is directed to the waste line.

21. The system according to claim 20, which comprises two sample loops, wherein the first sample loop retains a smaller volume of plating bath sample than the second sample loop and both sample loops are filled in the same, filling process.

22. The system according to claim 21, wherein the plating bath samples in the sample loops are sequentially moved to the analysis chamber via separate flow paths.

23. The system according to claim 20, wherein analysis of a plating bath sample is conducted simultaneously with the refilling of at least one sample loop.

24. A method for analyzing an analyte in a plating bath sample from an electrochemical deposition solution, the method comprising:

a) providing an analysis system comprising at least one analysis chamber, a sampling duct connected to an electrochemical processing tool, a four-way valve positioned between the electrochemical processing tool and the sampling duct, at least one carrier fluid duct connected to the analysis chamber, at least one actuatable multi-port valve that provides a transference platform between the sampling duct and the at least one carrier fluid duct, and a flow sensor connected



to the sampling duct and positioned downstream from the at least one actuatable multi-port valve;

b) flowing a sufficient amount of a plating bath sample from the electrochemical processing tool through the four-way valve into the sampling duct;

c) stopping the flow of the plating bath sample from the electrochemical processing tool when the flow sensor senses a sufficient amount of sample for testing in the analysis chamber; and

d) actuating the multi-port valve to transfer a predetermined amount of the plating bath sample from the sample duct to the carrier fluid duct for transference into the analysis chamber for analysis therein.